The Measurement of the Surface Areas of Milk Powders by a Permeability Procedure

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SUMMARY

Permeability apparatus and procedures have been developed that are capable of measuring the "smoothed" or "streamline" specific surface areas of milk powders and similar fragile materials. In addition, a method for determining the constant k in the Kozeny-Carman equation was derived and tested. The specific surface areas of a variety of milk powders measured by these procedures are reported.

INTRODUCTION

As part of an investigation of factors influencing the dehydration and rehydration of milk solids, the specific surface areas of milk powders produced by various drying techniques were measured by permeametry.

Permeability methods are known to give information on the extent of the "smoothed" or "streamline" surface areas of powder particles independent of areas resulting from surface cracks or pores.

The measurement of particle surface areas by permeability methods has been extensively studied and applied outside of the food field. For a compilation of references as well as a discussion of the underlying theory, consult Sullivan and Hertel (1942) and Orr and Dalla Valle (1959).

The relation between the surface area of a bed of closely packed particles and its permeability to fluid flow is given in the Kozeny-Carman equation:

$$Q = V/t = \frac{A}{YS^2} \times \frac{1}{k} \times \frac{\Delta p}{L} \times \frac{E^3}{(1-E)^2} \quad [1]$$

where:

Q = volume rate of fluid flow in the particle bed
V = volume of fluid flowing
t = time of V in sec
A = cross-sectional area of particle bed
Y = viscosity of fluid flowing
Δp = pressure drop across particle bed
L = height of particle bed
E = porosity of particle bed
k = "aspect" factor or shape factor
S = surface area/unit volume
P = air-free density of powder
S_w = specific surface = S/P

All terms except S and k can be arrived at by direct measurement.

This paper presents an indirect method for deriving appropriate k values for permeametric determination of the surface areas of milk powder produced by various drying techniques. Also presented is a description of a permeametry apparatus suitable for the study of milk powders and other similar fragile materials. The compression necessary to produce uniform powder beds in cells already described in the literature would cause powder breakage and fat extrusion incompatible with meaningful measurement. Surface areas of various
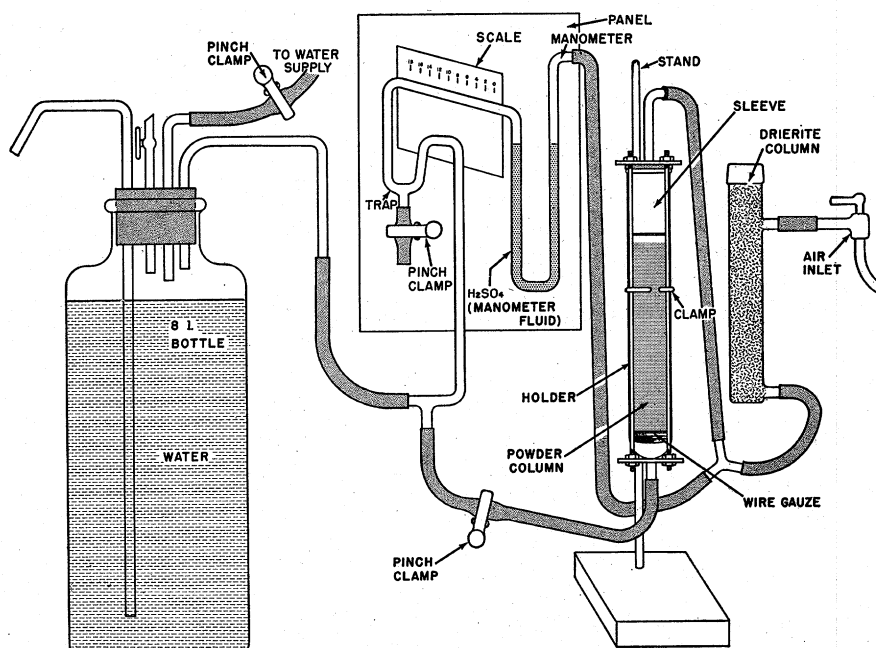

Fig. 1. Permeametry assembly for surface-area measurements of fragile food substances.
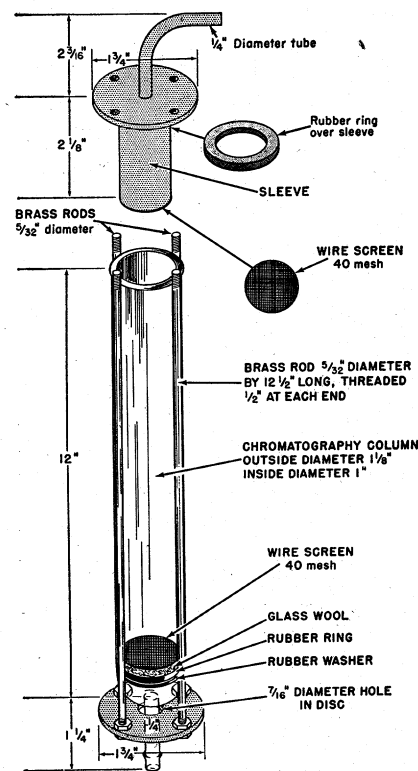

Fig. 2. Cell design for permeametry assembly of Fig. 1.

types of milk powders, measured as described, are reported.

MATERIALS

Samples of spray-dried nonfat and whole-milk powders were made with a 9-ft Swenson dryer (no endorsement implied) and conventional techniques. The spray-dried whole-milk foam was prepared with this dryer modified as described by Hanrahan *et al.* (1962). The vacuum-dried foams were made using the method reported by Sinnamon and his associates (1957). Commercial samples of milk powder were obtained in the local market. Letter designation indicates brand difference.

Permeametry. Fig. 1 shows the permeameter assembly, fabricated out of readily available material. Fig. 2 is a detail drawing of the permeametry cell. This drawing illustrates the supports and closure that enable use of a standard chromatography tube for the main body of the cell. The average cross-sectional area, A, of the tube used was 4.92 cm².

In this study, compressed air was the permeameter fluid. The air was passed through a column of Drierite before being forced through the powder column in the permeameter cell.

The pressure drop in the gas on passage through the column was measured with the manometer filled with concentrated H_2SO_4 (sp. gr. 1.82). The bent leg on the manometer increased its sensitivity. Constant pressure drop across the column was maintained manually with a valve in the incoming air line.

The volume of air flowing through the powder column was metered by the amount of water displaced from a large glass jar (cap. *ca.* 8 L). The volume of air was corrected for the vapor pressure of water at the temperature of the water used and for the pressure required to empty the container. The time, t, for the volume of water, V, to be emptied from the water jar was measured in seconds with an electric timer. The maximum rate of air flow used was 1.8×10^{-3} cfs.

The height, L, of the powder column in the permeameter cell was measured to the nearest mm at the pressure drop employed. Coarse milk powders, such as foam-dried and instant powders, were packed to heights of *ca.* 20 cm. A maximum column height of 6–8 cm was used for conventional spray-dried powders.

In surface-area calculations the viscosity of the permeameter fluid, Y (air at 25°C), was taken from the Handbook of Chemistry and Physics (1960).

The specific surface area, S_w, was

calculated from the slope of the line obtained by plotting $1/t$ versus Δp. This necessitates the use of a suitable k value describing the "aspect" or shape factors involved in formation of the particle bed.

This factor has been the subject of much investigation. Sullivan (1941, 1942) studied the relation between k and E by using bundles of cylindrical fibers oriented parallel to the direction of flow, and found that k depended on the porosity of the system, E. His results show that the porosity of a bed of particles is determined by factors implicit in the term k. The porosity, which is an index of the packing characteristics of a bed of particles, must depend upon the size, shape, density, and heterogeneity in these properties of the particles. These factors are also reflected in the value of k. Therefore, consideration of the directly determinable value of E should lead to the correct value of k for the type of powder under investigation.

The value of E for any powder bed can be calculated from the equation

$$E = 1 - \frac{W}{PAL} \qquad [2]$$

where all repeated terms have the meanings designated in the introduction of the Kozeny-Carman equation and W is equal to the weight of powder in the column. In calculations described in this paper, P was taken to be 1.31 g/cc for whole-milk powders and 1.44 g/cc for nonfat powders (Lea *et al.*, 1943).

In the Kozeny-Carman equation, E occurs in the complex expression $\frac{E^3}{(1-E)^2}$. This expression is abbreviated to $[E]$ and the entire equation is rearranged to the form:

$$1/t = \left[\frac{1}{k} \times \frac{A}{YVS^2} \times \frac{[E]}{L}\right]\Delta p \qquad [3]$$

From this it can be seen that the bracketed terms are equal to the slope of the line obtained from the plot $1/t$ versus Δp. Furthermore, the line can be expected to pass through the coordinate intercept if the experimental data are correct.

For the same powder, the values of the terms within the brackets are all fixed except L. The height of the particle bed can be varied experimentally, and the relation between L and the slope of the plot of $1/t$ versus Δp can be established. A plot of the slope versus L describes one segment of an equilateral hyperbola. In like manner, a plot of $[E]/L$ versus L also defines one segment of an equilateral hyperbola. Fig. 3 shows such hyperbolas,
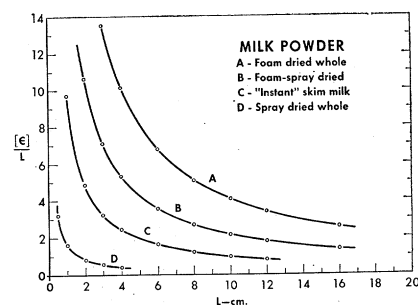

Fig. 3. The relation between porosity function, $[E]/L$, and the height of the powder column, L, for different milk powders.

derived from data obtained during a study of milk powders made by different drying techniques. The different hyperbolas are expressions of differences, related to both $[E]$ and k, in the packing properties of the powders. As stated previously, those factors controlling $[E]$ are inherent in the magnitude of k. Therefore, k can be considered a function of $[E]$ and expressed as:

$$k = f[E] \qquad [4]$$

In their derivation of the Kozeny-Carman equation, Fair and Hatch (1933) established that:

$$k = 2(L_e/L) \qquad [5]$$

where L, as designated, is the length of the powder column and L_e is the length of the tortuous path traversed by the permeametric fluid. It is taken as the shortest such path, and therefore is a limiting or minimum value such that:

$$k = \text{limit } f[E] = 2(L_e/L) \qquad [6]$$

A function of $[E]$ that has a limiting minimum value is the radius of curvature of the hyperbola $[E]/L$ at its vertex. It is assumed that a limiting value of a function, said function containing a parameter that is itself a limit, is the parameter or equal to it.

Equilateral hyperbolas are described by the equation:

$$xy = a \qquad [7]$$

Their radius of curvature is given by:

$$R_c = \frac{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}}{d^2y/dx^2} \qquad [8]$$

For the hyperbola:

$$\frac{dy}{dx} = \frac{-y}{x} \qquad [9]$$

$$\frac{d^2y}{dx^2} = \frac{2y}{x^2} \qquad [10]$$

Substituting these values in equation

8, the equation for radius of curvature becomes:

$$R_c = \frac{\left[1 + \left(\dfrac{-y}{x}\right)^2\right]^{3/2}}{\dfrac{2y}{x^2}} \quad [11]$$

At the vertex of an equilateral hyperbola, $y = x = \sqrt{a}$. Therefore, the minimum radius of curvature can be expressed as:

$$R_c \text{ min.} = \frac{[1+1]^{3/2}}{2/x} = \sqrt{2}\, x \quad [12]$$

The value of R_c min. in terms of $[E]$ is determined as follows:

$$x = \sqrt{[E]} \quad [13]$$

$$R_c \text{ min.} = \sqrt{2} \times \sqrt{[E]} = \sqrt{2[E]} \quad [14]$$

To develop a general method of determining the value of k from $[E]$, a unique value of $[E]$ must be first considered. Such a value is $[E] = 1$, which corresponds to an E value between 0.4 and 0.5. For this value of $[E]$ from equation 14:

$$R_c \text{ min.} = \sqrt{2} \quad [15]$$

Since this is a limiting value,

$$(L_e/L) = \sqrt{2} \quad [16]$$

The value of the ratio expressed in equation 16 corresponds to the length of the diagonal in a two-dimensional cell having unit sides and unit area.

If a column of powder particles forms, only unit cells, i.e., $[E] = 1$, then L_e and L of the limiting ratio L_e/L can be calculated. In a unit cell, $L_e = \sqrt{2}$. In a powder column containing n unit cells:

$$\text{Total } L_e = \overset{n}{\underset{}{\Sigma}}\, L_{ei} = nL_e = n\sqrt{2} \quad [17]$$

Again, by definition of a unit cell, $L = 1$. Therefore, in a powder column containing n unit cells:

$$\text{Total } L = \overset{n}{\underset{1}{\Sigma}}\, L_i = nL = n \quad [18]$$

and

$$(L_e/L) = \frac{n\sqrt{2}}{n} = \sqrt{2} \quad [19]$$

For the powder column that contains other than unit cells, $[E] \neq 1$, the cells present will be some multiple of the unit cell defined by $[E] = 1$. Then the ratio (L_e/L) for any cell can be given in terms of the defined unit cell. The value of (L_e/L) for powder columns containing other than unit cells can be calculated as follows:

a) Where $[E] < 1$, the number of small cells contained in a unit cell is given by the ratio of the radii of cur-

vature squared. Where R_o is the radius of curvature of the unit cell and R_i the radius of curvature of the cells considered:

$$\left(\frac{R_o}{R_i}\right)^2 = \left(\frac{1\sqrt{2}}{\sqrt{[E]}\,\sqrt{2}}\right)^2 = \frac{1}{[E]} \quad [20]$$

or

$$\frac{\text{no. of small cells}}{\text{unit cell}} = \frac{1}{[E]}$$

The diagonal of the small cells can be expressed as $a \times \sqrt{2}$ and the number of diagonals as $1/[E]$. The effective value of L_e for all little cells making up the unit cell can be considered as $\dfrac{1}{[E]} \times a \times \sqrt{2}$. Since the magnitude of one side of a unit cell is 1, the side of the unit cell can be defined in terms of the numbers of sides of the small cells it contains as being equal to

$$a \times \sqrt{\frac{1}{[E]}} \text{ or } a \times \frac{\sqrt{[E]}}{[E]}.$$

For the situation in which $[E] < 1$, the limiting ratio becomes

$$L_e/L = \frac{\dfrac{a\sqrt{2}}{[E]}}{\dfrac{a\sqrt{[E]}}{[E]}} = \sqrt{\frac{2}{[E]}} \quad [21]$$

b) Where the porosity of the powder column is such that $[E] > 1$, the number of unit cells contained in a cell, i, is given by the ratio of the radii of curvature squared.

$$\left(\frac{R_i}{R_o}\right)^2 = \left(\frac{\sqrt{2}\,\sqrt{[E]}}{\sqrt{2}}\right)^2 = [E] \quad [22]$$

The effective value of L_e of the cell i is the number of unit cells it contains times R_o, or $L_e = [E]\sqrt{2}$. One side of the cell, i, is of length $\sqrt{E}$. Therefore, for the case $[E] > 1$:

$$\left(\frac{L_e}{L}\right) = \frac{[E]\sqrt{2}}{\sqrt{[E]}} = \sqrt{2\,[E]} \quad [23]$$

Table 1. Areas of glass spheres and sand determined by permeametric and microscopic methods.

	Diameter	k	Area — m²/g	
			Permeametry	Microscope
Glass beads no. 110 [a]	200–230 μ	5.36	0.0110	0.0105
Glass beads no. 112	120–140 μ	5.28	.0183	.0185
Glass beads no. 117	44 μ	5.36	.0483	.0446
Ottawa sand	20–40 mesh	7.62	.0025	.0025 (as spheres)
				.0030 (as ellipsoids)

[a] The glass beads (Minnesota Mining and Milling Company) are designated by their commercial lot number.

Table 2. Areas of different kinds of milk powders as determined by permeametric methods.

Milk powder	k	Area (m^2/g)
Regular spray dried		
Commercial skim milk	2.94	0.259
Pilot-plant skim milk	4.88	.233
Instantized skim milk		
Commercial—A	9.40	.0397
B	9.27	.0372
C	7.84	.0525
D	8.8	.0571
Vacuum foam-dried 20 mesh		
Skim milk	12.6	.0523
Whole milk	18.1	.088
Foam spray dried		
Whole milk	11.33	.1050

RESULTS AND DISCUSSION

The permeametry apparatus and methods of calculations presented in this paper were tested by studying the specific surface area of glass beads of graded diameter. This allowed a check on the results by direct calculations based on microscopic measurements. Another model system, of impervious particles of increasing surface roughness, was Ottawa sand.

Table 1 shows specific surface areas of three lots of glass beads and the sample of sand. The microscopic areas were calculated from the weight fraction of each diameter of sphere within a lot. Although a narrow size distribution exists in each lot of glass spheres, the weight average area is still smaller than the number average area. It will be noted that a remarkably good agreement exists between the areas determined by microscopic and permeametric methods. The values of k used in the premeametry calculations were derived from the porosity expression as described above. The lack of uniformity of size and shape of the sand particles is expressed by the shifting k value.

Table 2 presents the "streamline" specific surface areas of the several different types of milk powders studied. From this table it can be seen that the conventional spray-drying technique produces particles that have a relatively high surface area as measured by permeametry. The compara-

tively small "smoothed" or "external" surfaces presented by the foamed and instantized materials must reflect a high degree of internal porosity with resultant low bulk density. The porosity of these particles, investigated by gas adsorption techniques, will be reported on in detail in a following paper.

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